INSTITUTE OF
PAPER CHEMISTRY
Appleton, Wisconsin

A FUNDAMENTAL STUDY OF COATING OF PAPER AND PAPERBOARD
STUDIES OF PORE STRUCTURE. I.

Project 2495

Report Four

A Progress Report

to

COATING RESEARCH GROUP

July 7, 1967

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A FUNDAMENTAL STUDY OF COATING OF PAPER AND PAPERBOARD

STUDIES OF PORE STRUCTURE. I.

SUMMARY

Internal replicas of the structure of pigment coatings have been made by allowing photosensitive ethylene dimethacrylate composition to penetrate into the coating and then photopolymerizing it by exposure to ultraviolet light. The paper and coating materials were removed by acid treatments and the plastic replicas examined by optical and electron microscopy.

The advancing fluid front could not be arrested before it reached the coating-paper interface with the ultraviolet light source available. Consequently, the gross contours of the arrested advancing front were those of the substrate surface. The scanning electron microscope at about 2000 diameters did not resolve the fine structure of the plastic replica. Attempts to prepare secondary replicas were complicated by the insolubility of the polymerized ethylene dimethacrylate, and the necessity to use a release agent to separate the secondary replica.

An unsupported starch-clay film was embedded in ethylene dimethacrylate and then cut at an oblique angle to the surface. The cut edge was polished and then etched to leave a plastic replica of the internal voids. Examination with the scanning electron microscope showed a scaly surface left by removal of the oriented clay platelets.

INTRODUCTION

The function of a pigment coating on a printing paper is to smooth the surface irregularities with a material of uniform and controlled absorptive properties for ink vehicle. Since the absorption properties are determined by the porous structure of the coating layer it is highly desirable to have means for pictorial representation of this porosity. The pore size of coatings is beyond the resolving power of the light microscope. Electron micrographs of surface replicas of coated papers provide some useful information but they are not able to provide a clear indication of the tortuous path which the advancing fluid front of the ink vehicle must follow. Ultrathin sections of coatings provide a clearer picture but since the sections must be much thinner than the dimensions of individual clay particles it is uncertain whether particles which might not be cemented to the other particles in the plane of the section have been lost from the coating specimen.

The present investigation was undertaken to evaluate the following scheme for studying the porous structure of paper coatings. If a polymerizable liquid which does not swell paper fibers or coatings is applied to the surface of a coated paper and then quickly polymerized, solid plastic will be formed on the coating surface and in the pores which had been filled with the liquid. Upon removal of the paper and coating components with acid an internal replica of the coating pores should remain which is bounded by the extent of capillary penetration at the time polymerization was effected.

In this study, ethylene dimethacrylate sensitized with benzoin was chosen as the polymerizable liquid because it increases in viscosity very rapidly as polymerization occurs and because it produces an insoluble polymer which is resistant to the acids needed to remove coating materials.

EXPERIMENTAL DETAILS AND RESULTS

PAPERS

The following three commercial coated papers were used:

(1) An uncalendered coated paper,

(2) A blade coated paper,

(3) A cast coated paper.

Sample sheets are included in the appendix. These sheets were embedded in methacrylate and cross sectioned. Photomicrographs of the cross sections of the papers are shown in Fig. 1. The structure of the coatings is not resolved by these photomicrographs even at higher magnification.

Figure 2 shows an electron micrograph of the cross section of the coating of the cast coated paper which was made by Miss Olga Smith of the Institute staff. An ultrathin section was used to permit transmission of electrons through the section. This electron micrograph gives a clear representation of the coating structure. However, since the thickness of the section (ca. 0.04 μm.) is only a fraction of the dimensions of the individual pigment particles, it is possible that the large open areas may have contained material which was not bonded to the other particles in the plane of the section.

POLYMERIZABLE LIQUIDS

Ethylene dimethacrylate photosensitized with 1% benzoin was used as the penetrating liquid. In some cases 5 or 10% of polymethylmethacrylate turnings (Rohm and Haas Plexiglass) was dissolved in the liquid to increase its viscosity. A drop of these liquids placed between microscope slides and exposed one inch from a Philips SP 500W mercury vapor lamp solidified to a solid film in 10 seconds.

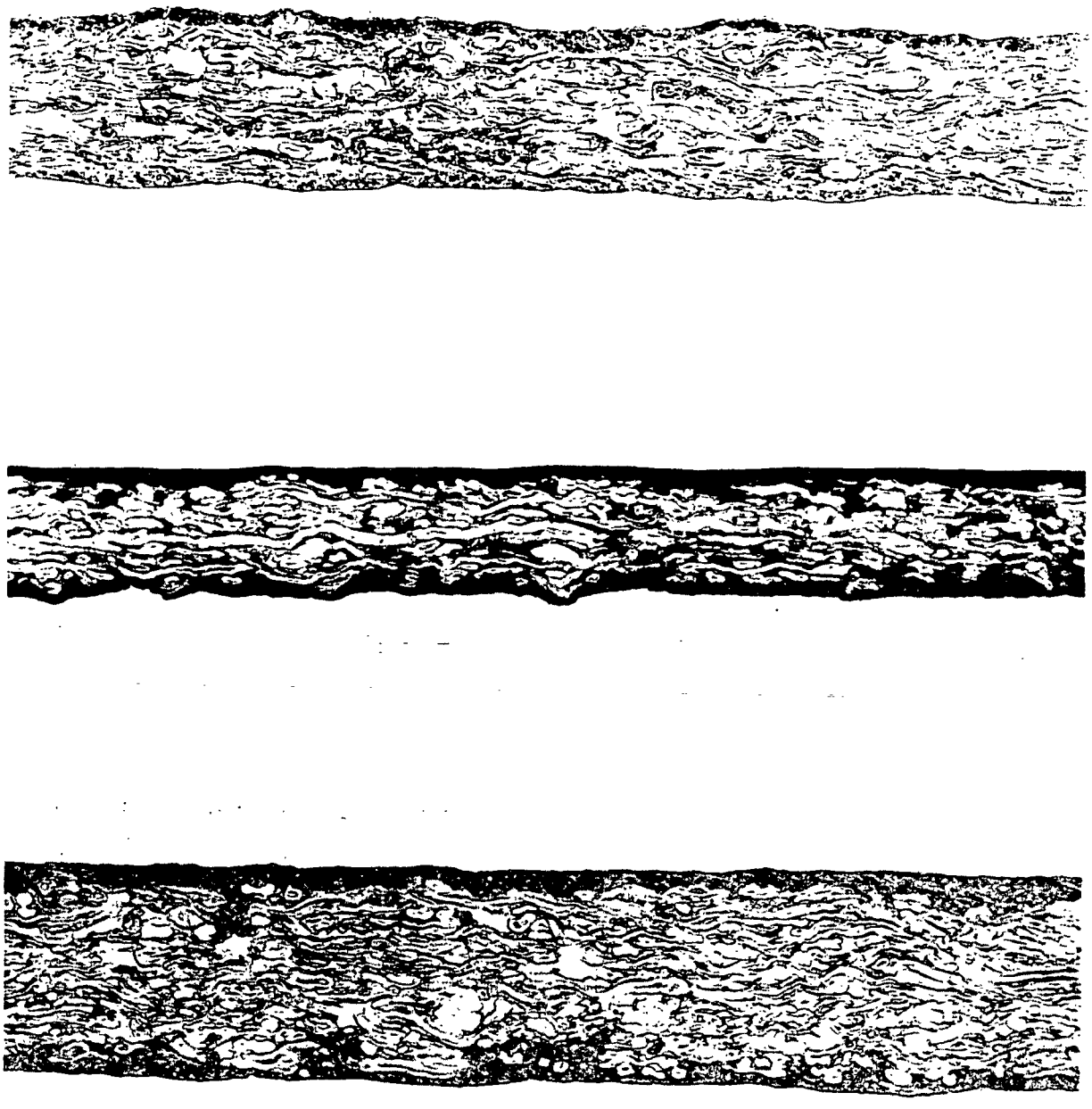

Figure 1. Coated Papers, Cross Section, 180X
A. Uncalendered Coated
B. Blade Coated
C. Cast Coated
(Methacrylate Embedments Sectioned and Mounted in Mineral Oil, Transmitted Light)

Figure 2. Cast Coating, Cross Section 4000X
(Ultrathin Section, Transmission Electron Microscope
Not Shadowed)

The rate of solidification was not noticeably changed by thickening the ethylene dimethacrylate with polymethylmethacrylate.

Some other polymerization initiators were tried in an effort to increase polymerization speed but none was found which was superior to benzoin. It was found possible to color the ethylene dimethacrylate with 2% of Du Pont Victoria Pure Blue BO without greatly reducing its rate of photopolymerization. This was done in some experiments in which extent of penetration was checked visually.

ATTEMPTS TO ARREST PENETRATION

The usual procedure was to place a drop of the polymerizable liquid on a microscope slide and invert the slide so the drop would hang over another slide on which the paper sample was supported. The upper slide was lowered to bring the liquid into contact with the paper and exposure to light was started. After an exposure of 10 seconds on each side, another application of thickened liquid was applied and exposure was repeated to build up a layer of plastic above the paper surface. Figure 3A shows the cross section of the coated, uncalendered paper with the impregnated coating and the attached plastic layer.

Paper and coating were removed from the plastic by immersion for 30 minutes in hot (90°C.) 9% HCl followed by 3.5 hours in 72% H_2SO_4 (18 to 22°C.) and then 30 minutes in 24% HF (25°C.). The replica was washed well with distilled water after each acid treatment. Examination of the plastic remaining after the acid treatments by x-ray diffraction showed no evidence of cellulose or crystalline pigment in the replicas prepared from the uncalendered coated paper or from the cast coated paper. The replica from the blade coated paper showed only a weak diffraction pattern which may have been due to traces of $CaSO_4$ or TiO_2.

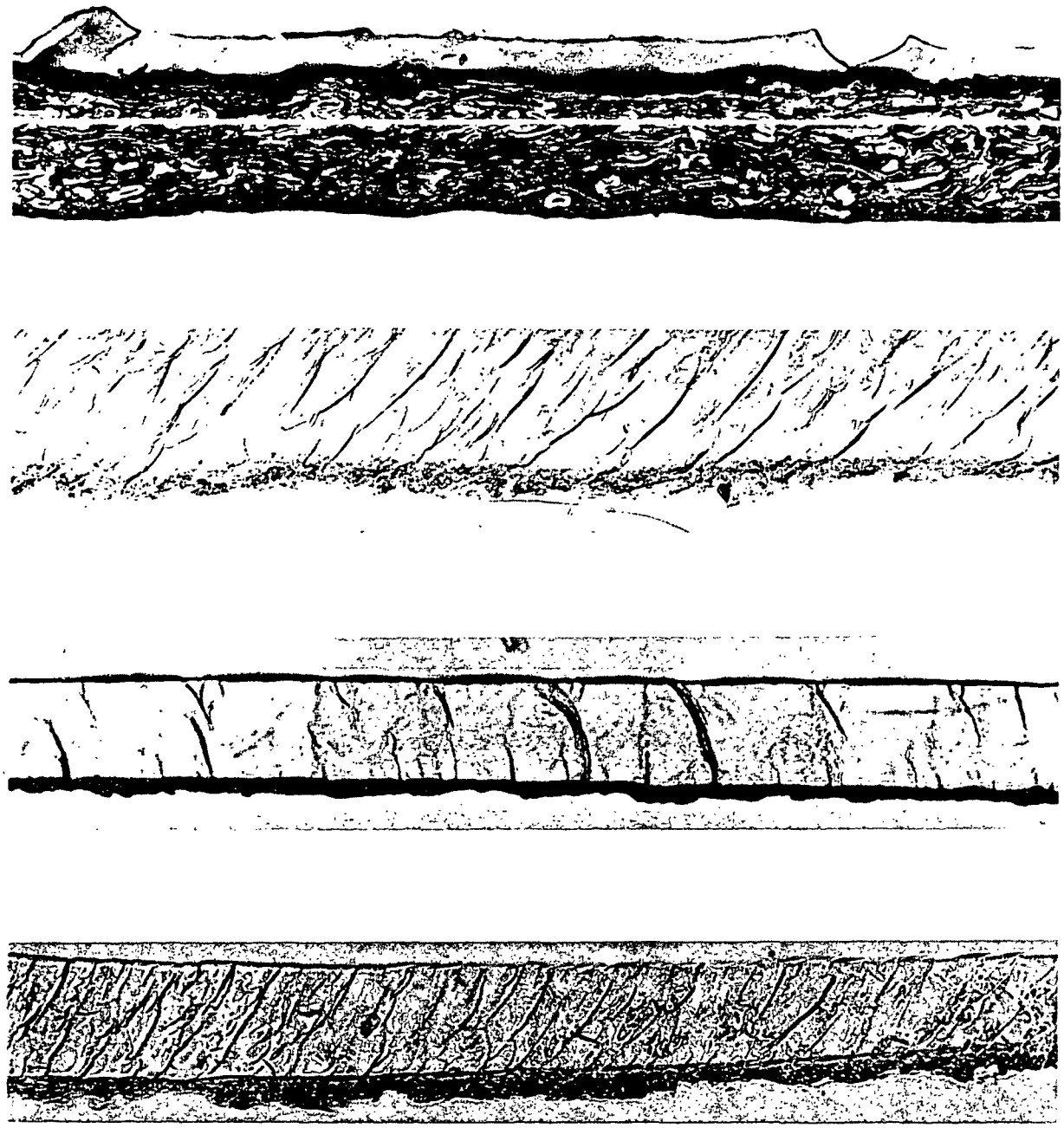

Figure 3. Coating Replicas, Cross Section, 180X
A. Uncalendered Coated - Before Dissolving Fiber and Coating Materials From Plastic
B. Uncalendered Coated
C. Blade Coated
D. Cast Coated
[Interrupted Penetration Replicas of Coatings (Except A), Embedded and Mounted in Mineral Oil, Transmitted Light]

Figure 3B, C, and D show cross sections of the pore replicas attached to the solid layer of plastic. Comparison of these with Fig. 3A and with Fig. 1 indicates that the plastic replica corresponds to the whole coating thickness with no detectable penetration into the raw stock. Figures 4 and 5A show photomicrographs of the surface of the replicas prepared from the three papers. In all cases the contours suggest that they are controlled by the surface of the raw stock.

In no case were replicas obtained in which the ethylene dimethacrylate had been polymerized before it reached the coating-raw stock interface. The liquid seemed to penetrate the coating quickly and accumulated at the interface. There was little tendency to penetrate the raw stock except at isolated spots where presumably pores of favorable size were available.

In the case of the blade coated paper it was possible to float the coating off with 72% H_2SO_4. The fragile isolated coating was carefully washed. Figure 5B shows the surface of this isolated coating which had been in contact with the raw stock. Comparison of Fig. 5A and B shows very similar gross contours and serves to establish that the ethylene dimethacrylate had penetrated to the coating raw stock interface before polymerization. In fine structure the solid material of the replica must correspond to the voids of the isolated coating.

In order to examine the fine structure of the replicas, electron micrographs were prepared for us by the Pulp and Paper Research Institute of Canada using their scanning electron microscope. The scanning electron microscope has the advantage that transmission of electrons through the specimen is not required so thicker samples can be examined without resorting to thin surface replicas. Figure 6 shows scanning electron micrographs of the blade coated and

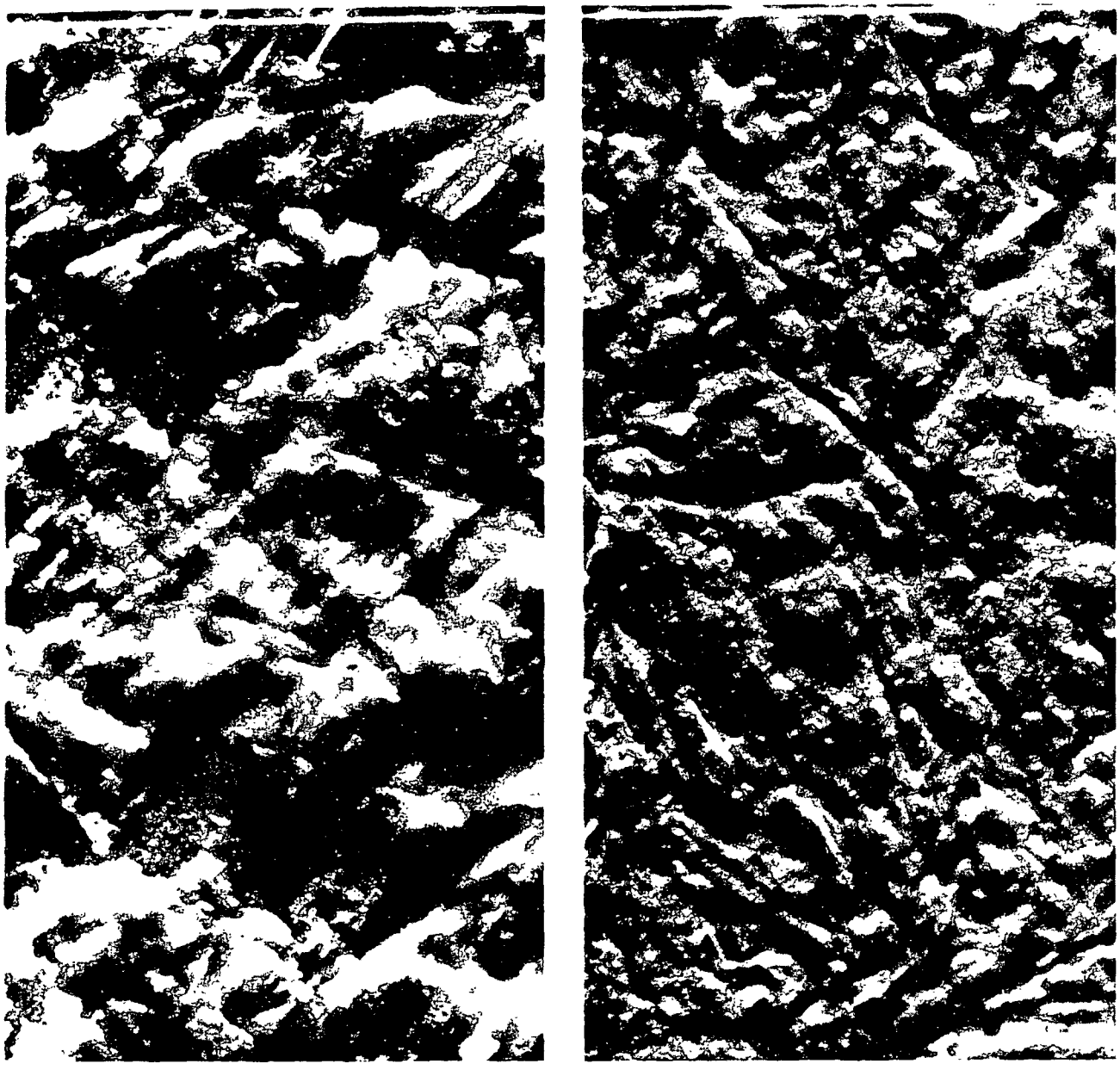

Figure 4. Coating Replicas, Interior Surface, 180X
A. Uncalendered Coated
B. Blade Coated
(Interrupted Penetration Replicas of Coatings, 85° Overstage Light)

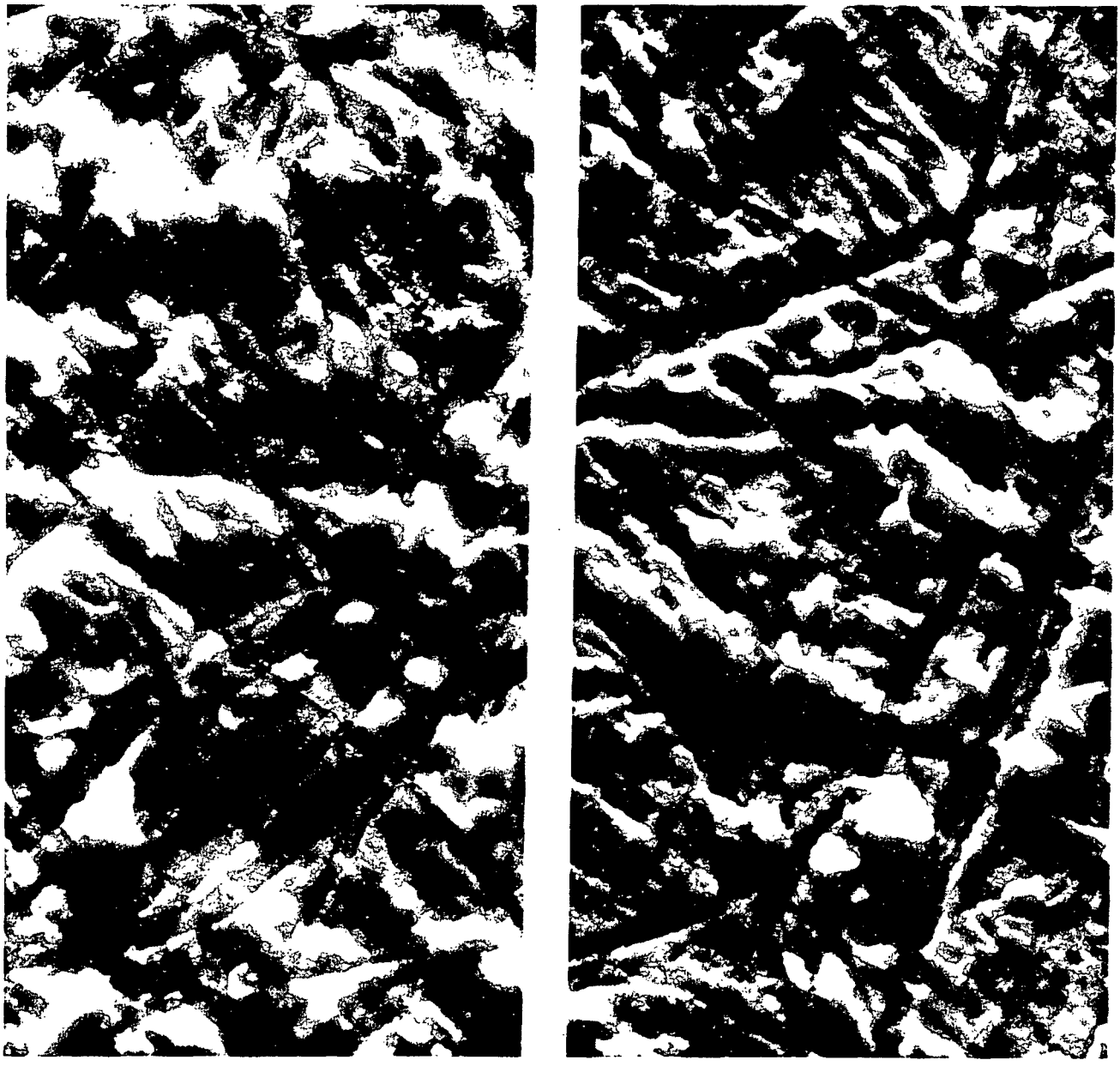

Figure 5. Cast Coating, Interior Surface, 180X
A. Replica (Interrupted Penetration)
B. Isolated Coating (Fibers Removed with 72% H_2SO_4)
(Both 85° Overstage Light)

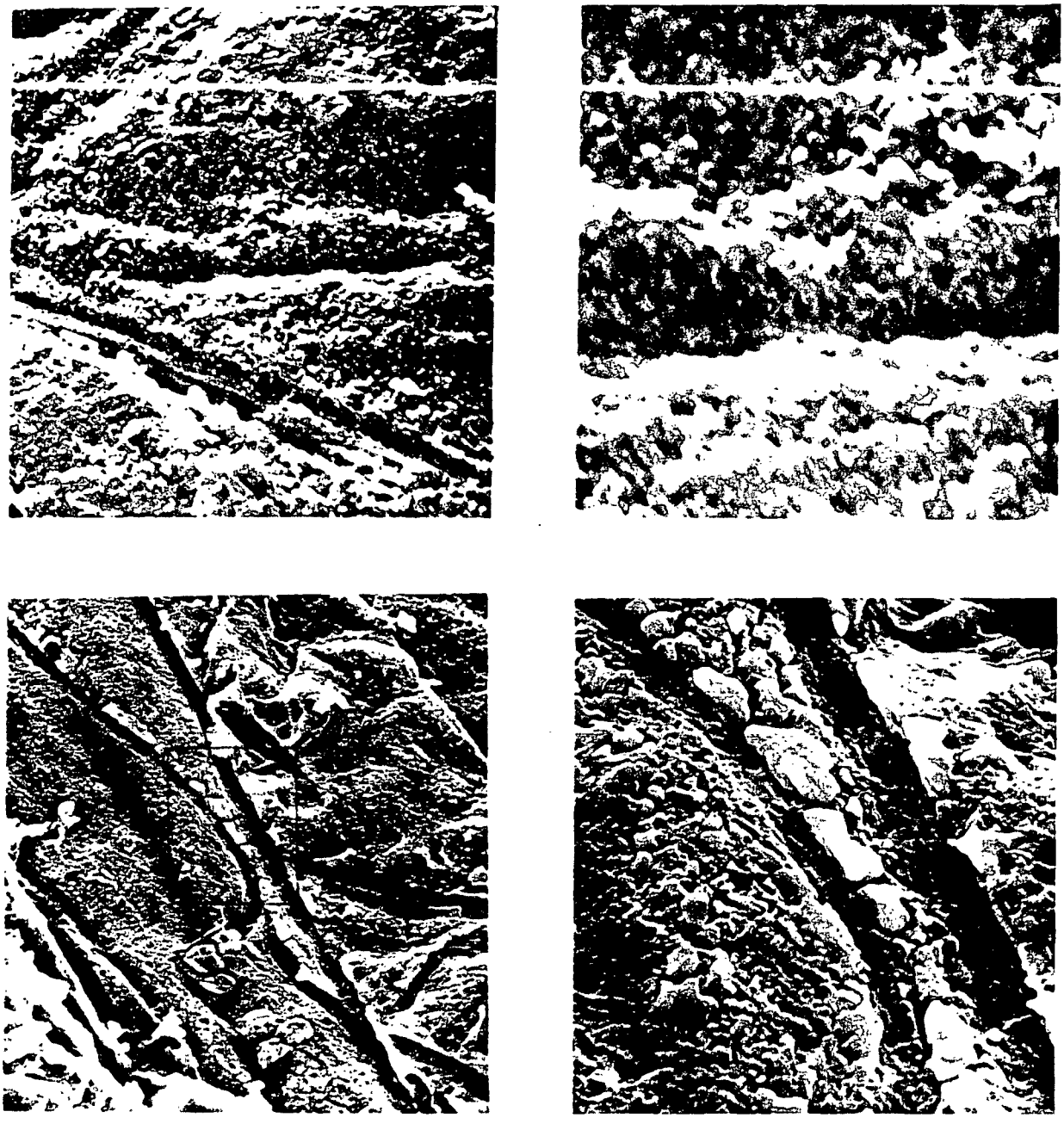

Figure 6. Coating Replicas, Interior Surface
A. Blade Coated, 636X
B. Blade Coated, 2080X
C. Cast Coated, 680X
D. Cast Coated, 2230X
(Interrupted Penetration Replicas, Scanning Electron Microscope)

cast coated pore replicas at two magnifications. These pictures reveal a rather striking difference in pore structure at the interface between the blade coated and the cast coated papers. However, even at the larger magnification the fine structure is not completely resolved.

In order to examine the surface of the internal replica at greater magnification, Miss Olga Smith prepared a secondary surface replica. Because of the difficulty in securing release of the replicating material it was necessary to use a release material. Figure 7 is an electron micrograph of the secondary replica for the cast coated paper. It is evident that much finer detail exists than was resolved by the scanning electron microscope. However, the detail is difficult to interpret in terms of coating porosity.

WORK WITH POLISHED SECTIONS

Since the ethylene dimethacrylate polymer proved to be so resistant to acid, some attempts were made to use it as an embedding material for polished and etched sections. In these experiments an unsupported clay starch film was impregnated with sensitized ethylene dimethacrylate, held between glass slides and exposed to the light from the mercury lamp. The encased sample was immersed in ethyl methacrylate containing 1% benzoyl peroxide and cured 16 hours at 50°C.

The embedded sample was polished at an oblique angle to the surface and then the surface was etched for 3 minutes with 5% HF solution.

Figure 8 shows scanning electron micrographs made at the Pulp and Paper Research Institute of Canada from this etched section. These micrographs indicate that the coating is layered due probably to the orientation of the platelike clay particles in the plane of the coating. When the clay is removed from the surface layers by etching with HF a scaly structure of plastic remains.

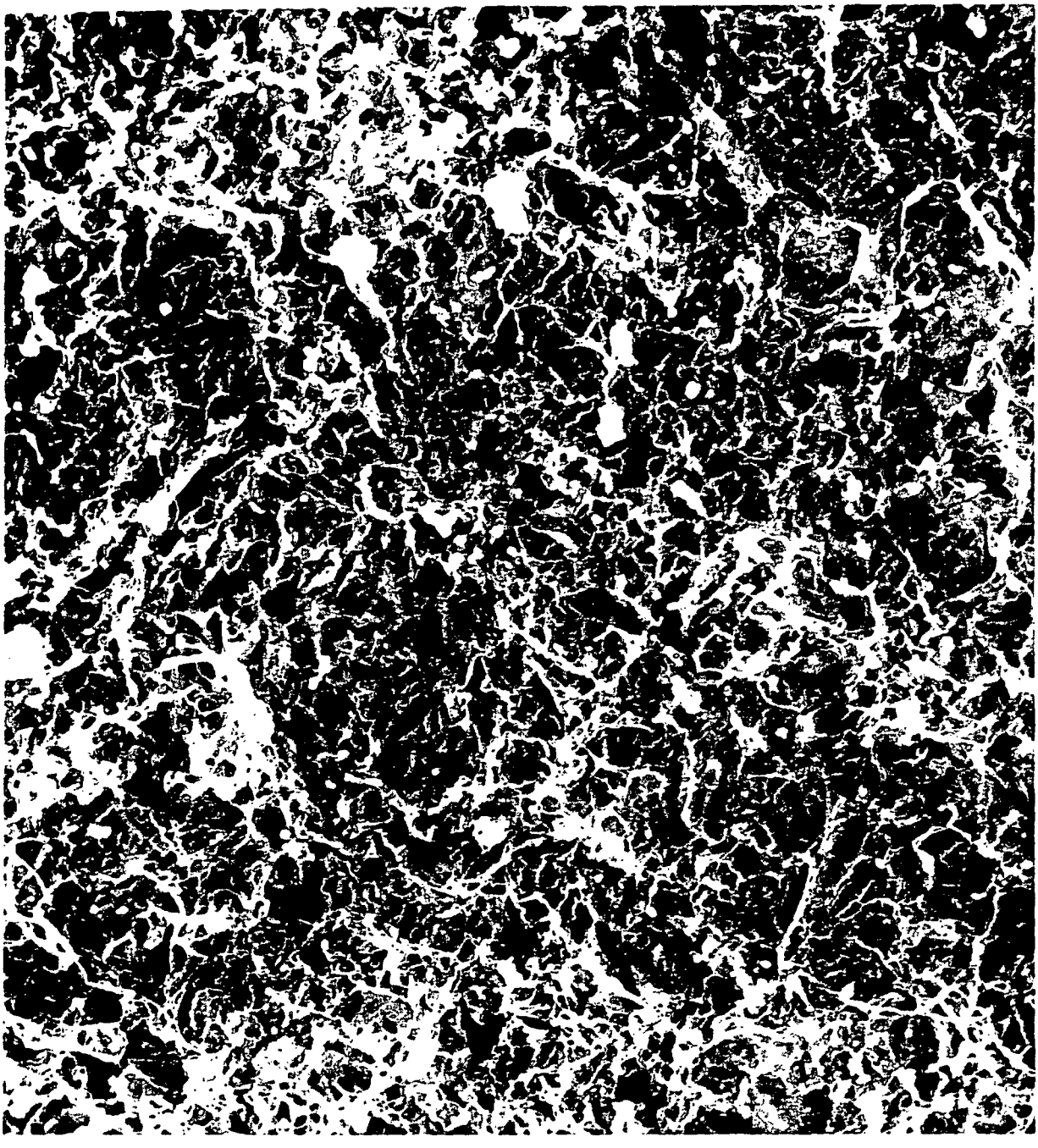

Figure 7. Cast Coating Replica, Interior Surface, 15,000X
(Interrupted Penetration Replica, Release Agents Used with Subsequent Negative Replica, Transmission Electron Microscope)

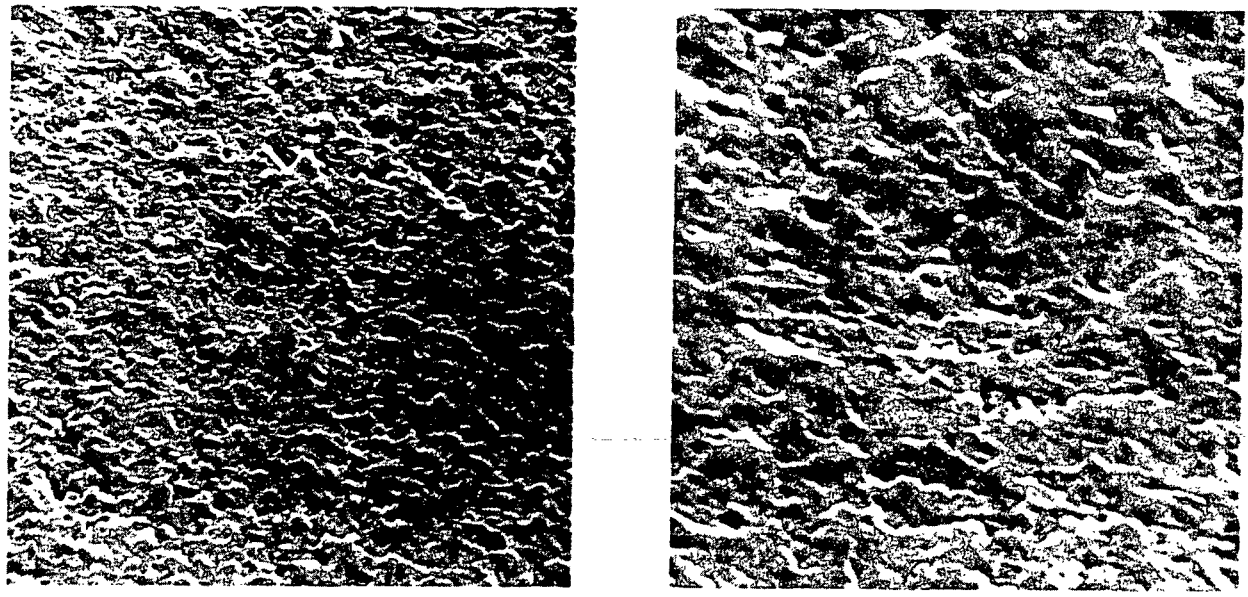

Figure 8. Unsupported Clay-Starch Coating, Etched Low-Angle Section
A. 2370X
B. 6460X
(Ethylene Dimethacrylate Embedment, Polished. Section Etched with 5% HF Solution, 3 min. Scanning Electron Microscope)

While ethylene dimethacrylate has the advantage of being very resistant to solvents and acids it has disadvantages in so far as the usual electron microscope techniques are concerned. It is too brittle for thin sectioning and so far no good way of making surface replicas from it have been developed.

POSSIBLE FUTURE WORK

While it has not been possible to trace the penetration of fluid through the capillary structure of the coating by the photopolymerization technique it still seems possible that this could be done if a more intense source of ultraviolet light were available. Sources do exist which can supply the necessary energy in a single flash of a few milliseconds. It is possible, however, that the qualities of the plastic formed might be different under such intense irradiation.

ACKNOWLEDGMENT

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THE INSTITUTE OF PAPER CHEMISTRY

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APPENDIX

PAPER SAMPLES ATTACHED

Cast

Coated

Blade

Coate

Coated,
Uncalendered